

# (12) UK Patent Application (19) GB (11) 2 224 031 (13) A

(43) Date of A publication 25.04.1990

(21) Application No 8921443.1

(22) Date of filing 22.09.1989

(30) Priority data

(31) 3832487

(32) 24.09.1988

(33) DE

(71) Applicant

Unifroyal Englebert Relfen GmbH

(Incorporated in the Federal Republic of Germany)

Postfach 410, Hüttenstrasse 7, 5100 Aachen 1,  
Federal Republic of Germany

(72) Inventor

Richard Michael Russell

(74) Agent and/or Address for Service

Potts Kerr and Co

15 Hamilton Square, Birkenhead, Merseyside,  
L41 6BR, United Kingdom

(51) INT CL<sup>4</sup>

C08L 9/06 7/00 // B60C 5/14

(52) UK CL (Edition J)

C3M MD M127 M128 M131C M133

B7C CKM

C3J JAC J364

U1S S1845 S3017 S3028 S3048

(56) Documents cited

GB 2198138 A GB 0983357 A GB 0786131 A

(58) Field of search

UK CL (Edition J) C3J JAC, C3M MD ML MXC

MXZ, C3V VDH VEA

WPI

(54) A pneumatic vehicle tyre

(57) In a pneumatic vehicle tyre, the rubber inner layer is formed from an adhesive rubber and styrene-butadiene copolymers, wherein the content of styrene, which is bound in the molecule, in the blended mixture is at least 15 parts by weight per hundred parts of rubber. A low gas-permeability and sufficient mechanical strength are hereby attainable for the rubber inner layer. The production of the pneumatic vehicle tyres, which have an initially cross-linked or partially cross-linked rubber mixture for the inner layer, is possible because the tyre is vulcanised without a bellows. The costs for the raw materials and for the production method can therefore be considerably reduced.

A pneumatic vehicle tyre.

The invention relates to a pneumatic vehicle tyre having a carcass, more especially a radial carcass, which is provided with textile reinforcing members, and having an inner layer of low gas-permeability, which extends radially with respect to the carcass and is formed from a vulcanisable rubber mixture.

In pneumatic vehicle tyres, the tyre interior is formed by a rubber layer of low gas-permeability situated radially within the carcass and ensures that the compressed air, with the required pressure value and the necessary air volume, permits the tyre to operate reliably when viewed over a long period of time.

Vulcanisable rubber mixtures containing halobutyl are utilised as rubber inner layers of low gas-permeability. Low gas-permeability values can thus be attained, measured in  $\frac{\text{M}^2}{\text{S.Pa}} \cdot 10^{-17}$ , which ensure the required air pressure and volume values for the pneumatic vehicle tyre when viewed over a long period of time. However, the vulcanisable rubber mixtures, which contain halobutyl or are formed therefrom, have a relatively low mechanical strength.

The object of the invention is to develop a rubber inner layer of low gas-permeability for this type of tyre in such a manner that it has a high mechanical strength and also attains gas-permeability values which are comparable with those of the rubber layers containing halobutyl.

Furthermore, the rubber mixture for the inner layer of the tyre should be initially or partially cross-linkable, and the pneumatic tyres should be vulcanisable without a heating bellows as a result of such an inner layer.

In accordance with the invention there is provided a pneumatic vehicle tyre having a carcass, more especially a radial carcass, which is provided with textile reinforcing members, and having an inner layer of low gas-permeability, which extends radially with respect to the carcass and is formed from a vulcanisable rubber mixture in which the inner layer is formed from a blended mixture of at least one styrene-containing, emulsion- or solution-polymerised styrene-butadiene copolymer and from at least one adhesive rubber, wherein the content of styrene, which is bound in the molecule, is at least 15 parts by weight per hundred parts of rubber.

The blended rubber mixture also contains conventional reinforcing fillers, as well as vulcanising agents and micro-chemicals.

Because there is a relatively small content of bound styrene in the region of at least 15 parts by weight per hundred parts of rubber in the blended rubber mixture, a mechanical strength is achieved, on the one hand, for the rubber inner layer which is at least in the region of 10 MPa, and a relatively low gas-permeability value is also achieved, on the other hand, in the region of  $3 \frac{\text{M}^2}{\text{S.Pa}} \cdot 10^{-17}$ . These two properties ensure that the compressed air values and compressed air volumes permit the tyre to operate reliably when viewed over a long period of time.

Because of the above-mentioned, relatively small styrene content in the blended mixture for an inner layer, this mixture can only advantageously be partially or initially or prevulcanised in operational terms. A membrane-like, sufficiently strong skin is thus formed. In consequence, a vulcanisation method without bellows is possible with additional advantages.

The initial cross-linking may be achieved by conventional means in the form of sulphur accelerator systems or by electron radiation. In such a case, the rubber mixture does not become decomposed as a result of the effect of the electron beams, such as is the case with a rubber mixture containing butyl.

The method of electron radiation is known, compare in this connection the journal entitled "Elastomeric", 117 (11) 34, 1985, and the use of electron radiation for producing rubber mixtures is known from DE-A-37 05 761.

The rubber mixture with a relatively small bound styrene content for the rubber inner layer may be initially cross-linked either as a separate rubber layer or as a component part of the unvulcanised tyre. The strong form of the membrane-like skin of the initially cross-linked inner layer assumes the function of the heating bellows.

In such a case, vulcanisation without a heating bellows presents considerable advantages in terms of a saving in energy and in the production means, namely the bellows and its accessories.

Smaller material and production costs are required. The heating period is shortened, and the tyre output figures are increased when compared with the standard method of vulcanisation utilising a heating bellows.

The additional advantages of the rubber mixture with a relatively small styrene content are its simple, operational processability and its good adhesive strength with respect to the adjacent carcass ply.

This rubber inner layer is preferably to be combined with a carcass ply, whereby there is a relatively small content of at least 20 parts by weight of bound styrene per hundred parts of rubber. Similar rubber mixtures according to DE-A-36 36 783 and 37 41 722 have been proposed for the carcass. Just like the mixture for the inner layer, the blended mixture for the carcass ply has a bound styrene content of at least 20 parts by weight per hundred parts of rubber and is initially or partially cross-linkable either by means of heat and pressure with the utilisation of sulphur accelerator systems or by means of electron radiation. The additional advantages which are achieved reside in reducing the costs for the raw materials, improving the operational processability, providing the adjacent plies with a high degree of adhesion with respect to one another, and improving the mechanical strength. Advantageous gas-permeability values are achieved, which are comparable with those achieved by combining the materials of the carcass ply and a butyl inner layer.

20

The invention is explained with reference to embodiments, the inner layer of the invention being compared with a known inner layer, and comparable values for carcass plies also being mentioned.

25

Table 1

Composition of the rubber mixture  
100 parts weight per hundred parts  
rubber weight

Rubber mixture	A	B	C	D
	Inner layer	Carcase	Inner layer	Carcase
Styrene-butadiene copolymer 1500	30	20	-	30
Styrene-butadiene copolymer 1013	25	40	-	-
Bound styrene	18	22	-	7
Natural rubber	45	40	40	50
Polybutadiene	-	-	-	20
Chlorobutyl	-	-	60	-
GPF N-660 carbon black	65	85	41	45
Aromatic oil	22	9	6	8
Gas-permeability	$\frac{M^2}{5.Pa} \cdot 10^{-17}$			
30°C	3.5	3.6	1.7	8.6
50°C	8.3	8.9	4.7	21.0
70°C	17.3	18.1	10.0	37.0
Mechanical strength MPa	10.5	14.3	6.1	12.6

Table 2

	Pneumatic vehicle tyre 1	Pneumatic vehicle tyre 2	Pneumatic vehicle tyre 3
Tyre size	205/65 VR 15	205/65 VR 15	205/65 VR 15
Type	tubeless	tubeless	tubeless
Carcase rubber mixture	D	B	B
Inner layer rubber mixture	C	B'	A
Loss of compressed air per day 0.1 bar at 35°C	18	21	20

Remark: The rubber mixture B' corresponds to the rubber mixture B for a carcass mixture which is utilised here as the mixture for the inner layer.

When the rubber mixture A of the invention is compared with a known rubber mixture C, it is apparent that the inner layer, which is produced from the rubber mixture A comprising styrene-butadiene copolymers and natural rubber with a bound styrene content of 18 according to Table 1, has the gas-permeability values of 3.5, 8.3 and 17.3 - compare the relevant column - and the mechanical strength value of 10.5 MPa - compare the relevant column. However, the known inner layer according to rubber mixture C, which comprises chlorobutyl and natural rubber, has the gas-permeability values of 1.7, 4.7 and 10.0 and a strength value of 6.1 MPa.

The gas-permeability of the inner layer of the tyre is sufficiently good, and the strength is considerably improved.

It is apparent from Table 2 that, by combining a carcass ply with the inner layer formed from a rubber mixture of the invention, the values for the loss of air from the tyre are comparable with the values of the known embodiment. However, the carcass ply and the inner layer have the additional, significant advantages that considerably reduced costs are achieved for the raw materials and production method, and that a substantially more advantageous, operational processability of the raw materials is provided. On the whole, therefore, the costs are less than those for a rubber layer containing chlorobutyl. The additional advantages of the inner layer formed from a rubber mixture of the invention are its improved mechanical strength and its high adhesive strength with respect to the adjacent carcass ply. The rubber mixture of the invention is initially or partially cross-linkable, so that a sufficiently strong membrane-like skin is hereby produced, which permits the unvulcanised tyre, provided with such an initially cross-linked inner layer, to be used for the vulcanisation of pneumatic vehicle tyres without utilisation of a bellows.

The rubber mixture, containing the styrene-butadiene copolymer component, is preheated, for example, at a temperature of 150°C for approximately five minutes. It then forms a membrane-like skin, as mentioned above. This is sufficiently strong and impermeable, so that it can absorb the heating medium of water and/or vapour during the vulcanisation of a tyre without a bellows. In this case, the previously treated inner layer of the unvulcanised tyre assumes the function of the heating bellows.

The blended rubber mixture, which contains the styrene-butadiene copolymer component and has a small styrene content, is also suitable for being initially cross-linkable by means of electron radiation. In such a



case, energy concentrations of approximately 2 to 16 M rad are suitable for solidifying the rubber mixture to form a membrane-like skin so that, even in this case, the previously treated inner layer of the unvulcanised tyre can assume the function of the heating bellows. The radiation treatment may be effected in such a manner that either the inner layer ply in the region of the production process in the calender is subjected to a radiation field, or the inner layer of the already built, unvulcanised tyre is locally radiated by electrons. Because vulcanisation is achieved without a bellows, the entire method for vulcanising pneumatic vehicle tyres can be accomplished with the above-mentioned advantages.

CLAIMS

1. A pneumatic vehicle tyre having a carcass, more especially a radial carcass, which is provided with textile reinforcing members, and having an inner layer of low gas-permeability, which extends radially with respect to the carcass and is formed from a vulcanisable rubber mixture, in which the inner layer is formed from a blended mixture of at least one styrene-containing, emulsion- or solution-polymerised styrene-butadiene copolymer and from at least one adhesive rubber, wherein the content of styrene, which is bound in the molecule, is at least 15 parts by weight per hundred parts of rubber.
2. A pneumatic vehicle tyre as claimed in claim 1, in which the inner layer is combined with a carcass ply which is formed from at least one styrene-butadiene copolymer and at least one adhesive rubber, wherein the content of styrene, which is bound in the molecule, is at least 20 parts by weight per hundred parts of rubber.
3. A pneumatic vehicle tyre as claimed in claim 1 or 2, in which the rubber mixture of the inner layer is a rubber mixture which is partially vulcanisable or initially vulcanisable by means of a sulphur accelerator system as a result of pressure and heat.
4. A pneumatic vehicle tyre as claimed in claim 1 or 2, in which the rubber mixture of the inner layer is a rubber mixture which is partially vulcanisable or initially vulcanisable by means of electron radiation.

5. A pneumatic vehicle tyre as claimed in claim 3 or 4, in which the inner layer is partially or initially vulcanisable as a component part of the tyre.
- 5 6. A pneumatic vehicle tyre as claimed in claim 3 or 4, in which the inner layer of the unvulcanised tyre is partially or initially vulcanisable.
- 10 7. A pneumatic vehicle tyre as claimed in claim 2, in which the blended mixture for the carcass ply, having a bound styrene content of at least 20 parts by weight per hundred parts of rubber, is partially or initially vulcanisable.
- 15 8. A pneumatic vehicle tyre, as claimed in any preceding claim, substantially as hereinbefore described.
- 20 9. A method of vulcanising a pneumatic vehicle tyre as claimed in claims 1 to 8, in which the unvulcanised tyre, having an inner layer which is in the form of a strong inner skin as a result of initial or partial cross-linking, is introduced into the vulcanising press and, when the vulcanising press is closed, absorbs the vulcanising pressure medium, which is in the form of hot water and/or vapour, without a heating bellows, and this unvulcanised
- 25 tyre is vulcanised as a result of pressure and heat.
- 30 10. A method of vulcanising a pneumatic vehicle tyre as claimed in claim 9, substantially as hereinbefore described.

THIS PAGE BLANK (USPTO)